

No separate roles of repulsive and attractive pair forces for the physics of liquids

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(Dated: August 21, 2012)

According to standard liquid-state theory repulsive and attractive pair forces play distinct roles for the physics of liquids. We here present a continuous series of pair potentials that have virtually the same structure and dynamics, although only some of them have attractive forces. This reflects the fact that the motion of a given particle is determined by the total force on it, not the individual contributions to the force from other particles, which in terms of the pair potential is the quantity usually discussed in liquid-state theory.

A liquid is held together by attractions between its molecules. It is very difficult to compress a liquid because the molecules strongly resent closely approaching each other. These facts have been well known for a long time, and today it is textbook knowledge that the repulsive and the attractive forces play distinct roles for the physics of liquids. The repulsive forces, which ultimately derive from the Fermi statistics of electrons, are harsh and short ranged. According to standard theory these forces are responsible for the structure and, in particular, for reducing considerably the liquid’s entropy compared to that of an ideal gas at the same density and temperature. The attractive forces, on the other hand, are long ranged and weaker. The attractions, which derive from induced dipolar interactions, reduce the pressure and energy compared to that of an ideal gas at the same density and temperature. We argue below that this picture, though very appealing, overemphasizes the individual pair forces and does not provide a full understanding, because systems may be constructed where the repulsive and attractive interactions clearly do not play separate roles.

The traditional understanding of the liquid state is based on pioneering works by Frenkel, Longuet-Higgins and Widom, Barker and Henderson, and Weeks, Chandler, and Andersen (WCA), and many others [1, 2]. The fundamental idea is that the attractions may be regarded as a perturbation of a Hamiltonian based on the repulsive forces, the physics of which is usually well represented by a hard-sphere reference system [3]. Perturbation theories based on this picture [1–4] are standard for calculating simple liquids’ thermodynamics and structure as quantified by the radial pair distribution function $g(r)$. We do not question these very useful perturbation theories, but argue below from theory and simulations that the repulsive and the attractive pair forces do not always play clearly distinguishable roles for the structure and dynamics of simple liquids.

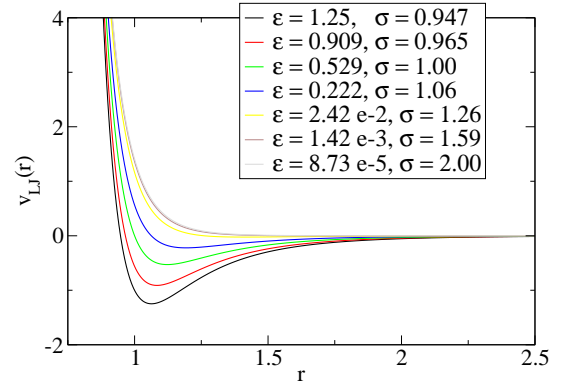


FIG. 1: Lennard-Jones pair potentials $v_{LJ}(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$ predicted to give the same physics at the state point $(\rho, T) = (1, 1)$. Visually these potentials have little in common; in particular, they have very different contributions from attractive forces. The pair potentials were constructed analytically using the isomorph theory (detailed in the text after Fig. 2).

This point is illustrated in the simplest possible way by studying systems of Lennard-Jones (LJ) particles. The LJ pair potential is given by $v_{LJ}(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$, where ϵ and σ specify the energy and length scales, respectively. It is shown below that the different LJ pair potentials of Fig. 1 give rise to virtually the same structure and dynamics at the state point $(\rho, T) = (1, 1)$ (this defines the unit system used below and is the unit system in which the ϵ ’s and σ ’s of Fig. 1 are given). The potentials of Fig. 1 all have attractive forces, but for some of the potentials the attractive forces are insignificant. To show that these potentials have the same structure and dynamics, NVT computer simulations of systems of 1,000 particles were performed using our RUMD software, which runs on graphical processing units [5].

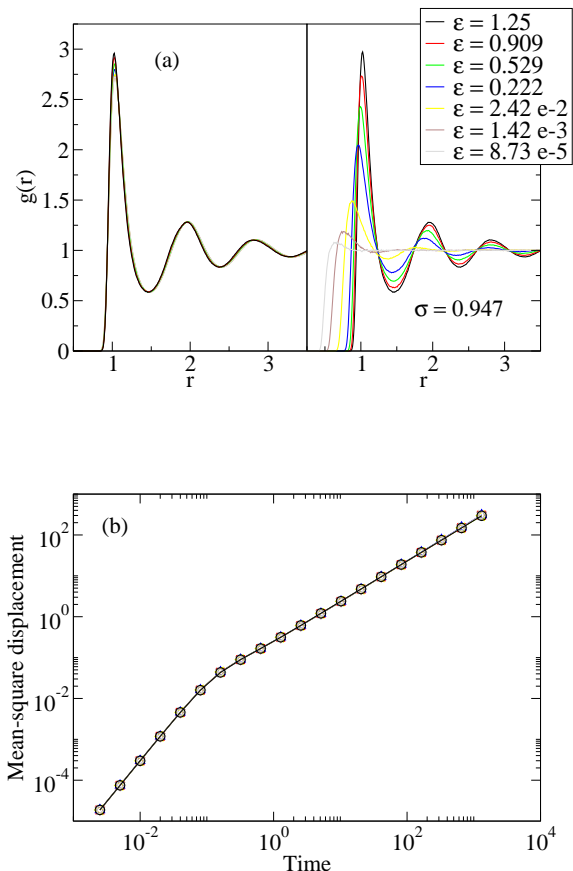


FIG. 2: (a) The radial pair distribution function for the LJ pair potentials of Fig. 1 at the state point $(\rho, T) = (1, 1)$ (left panel) and for a series of LJ pair potentials with fixed σ parameter (right panel) at the same state point. (b) The mean-square displacement for the LJ pair potentials of Fig. 1 at the state point $(\rho, T) = (1, 1)$.

Figure 2(a) (left panel) shows the radial distribution function $g(r)$ for the seven LJ pair potentials of Fig. 1 at the state point $(\rho, T) = (1, 1)$. For comparison, simulations are shown in the right panel for seven potentials with the same ϵ variation, but fixed $\sigma = 0.947$. Figure 2(b) shows the mean-square displacement for the Fig. 1 potentials. By the Henderson uniqueness theorem [6] the pair potentials of Fig. 1 cannot have exactly the same pair distribution functions, but clearly they do have lead to very similar structure and dynamics.

How were the pair potentials of Fig. 1 determined, and why do they have the same structure and dynamics? The starting point is the existence of isomorphs in the phase diagram of liquids with strong correlations between NVT virial and potential-energy equilibrium fluctuations [7, 8] (which we recently argued is a useful definition of a “simple” liquid [9]). Two state points with density and temperature (ρ_1, T_1) and (ρ_2, T_2) are termed isomorphic [7] if all pairs of physically relevant micro-

configurations of the two state points, which trivially scale into one another [i.e., $\rho_1^{1/3} \mathbf{r}_i^{(1)} = \rho_2^{1/3} \mathbf{r}_i^{(2)}$ for all particles i], have proportional configurational Boltzmann factors. This means that $\exp[-U(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_N^{(1)})/k_B T_1] = C_{12} \exp[-U(\mathbf{r}_1^{(2)}, \dots, \mathbf{r}_N^{(2)})/k_B T_2]$. LJ systems are strongly correlating and thus have isomorphs to a good approximation [8]. The invariance of the canonical probabilities of scaled configurations along an isomorph has several implications [7]: Excess entropy and (excess) isochoric specific heat are both isomorph invariant, the dynamics in reduced units are invariant for both Newtonian and Brownian equations of motion, reduced-unit static density correlation functions are invariant, a jump between two isomorphic state points takes the system instantaneously to equilibrium, etc. For Newtonian dynamics using reduced units corresponds to measuring length in units of $\rho^{-1/3}$, time in units of $\rho^{-1/3} \sqrt{m/k_B T}$ where m is the particle mass, and energy in units of $k_B T$. Thus the reduced particle coordinates are defined by $\tilde{\mathbf{r}}_i = \rho^{1/3} \mathbf{r}_i$.

Recently it was shown that liquids with good isomorphs have simple thermodynamics in the sense that the temperature is a product of a function of excess entropy per particle s and a function of density [10],

$$T = f(s)h(\rho). \quad (1)$$

The function $h(\rho)$ inherits the analytical structure of the pair potential in the sense that if the latter is given by the expression $v(r) = \sum_n v_n r^{-n}$, then $h(\rho) = \sum_n C_n \rho^{n/3}$ in which each term corresponds to a term in the pair potential. Since $h(\rho)$ is only defined within an overall multiplicative constant, one can write for the LJ pair potential

$$h(\rho) = \alpha \rho^4 + (1 - \alpha) \rho^2. \quad (2)$$

The constant α was determined from simulations at the reference state point $(\rho, T) = (1, 1)$ for $\epsilon = 1.25$ and $\sigma = 0.947$, which is a typical liquid state point of the LJ system. This was done by proceeding as follows [11]. We have previously [7, 10] derived the identity

$$\gamma \equiv \left(\frac{\partial \ln T}{\partial \ln \rho} \right)_s = \frac{d \ln h}{d \ln \rho} = \frac{\langle \Delta W \Delta U \rangle}{\langle (\Delta U)^2 \rangle}, \quad (3)$$

in which W is the virial, U the potential energy, and the angular brackets denote NVT ensemble averages. The physical interpretation of γ (which varies with state point) is that $n = 3\gamma$ is the exponent of the inverse-power-law potential approximately reproducing the behavior at the state point in question. Combining Eq. (2) with Eq. (3) and the simulation results for the fluctuations of W and U leads to $\alpha = \gamma/2 - 1 = 1.85$. Note that the ρ^2 term of Eq. (2) is thus negative, which reflects the attractive r^{-6} term of the LJ potential.

An isomorph is a set of state points with invariant structure and dynamics in reduced units [7]. Via appropriate rescaling, however, an isomorph can be interpreted differently: as defining a set of *different* LJ pair potentials that give invariant properties at the *same state point*. These are simply two different ways of looking at an invariant Boltzmann factor: Using the unit system where $k_B = 1$, Eq. (1) implies that $\exp(-U(\rho^{-1/3}\tilde{\mathbf{r}}_1, \dots, \rho^{-1/3}\tilde{\mathbf{r}}_N)/[f(s)h(\rho)]) = \exp(-[1/f(s)] \sum_{i<j} v_{\text{LJ}}(\rho^{-1/3}\tilde{r}_{ij})/h(\rho))$ where r_{ij} is the distance between particles i and j . Along an isomorph $f(s)$ is a constant; if we consider the isomorph which includes the state point $\rho = T = 1$, then given the normalization of Eq. (2) we have in fact $f(s) = 1$. The shift in interpretation now comes by noticing that the same Boltzmann factor is obtained by considering a configuration at unity density and unity temperature and a family of *isomorphic pair potentials* $v_{\text{LJ}}^d(r) \equiv v_{\text{LJ}}(d^{-1/3}r)/h(d)$, where we have dropped the tilde from positions and replaced ρ with d to emphasize the shift in perspective. These pair potentials are still LJ potentials, but with different energy and length parameters. These are the potentials plotted in Fig. 1. .

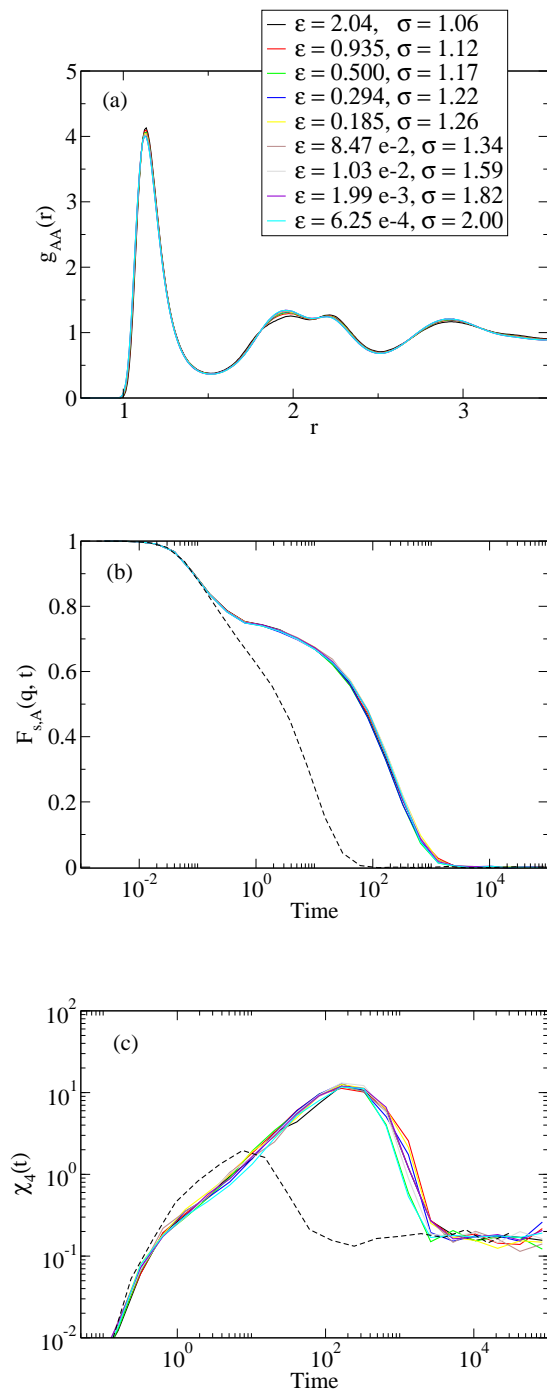


FIG. 3: (a) The AA particle radial distribution function of the Kob-Andersen binary Lennard-Jones mixture for a family of isomorphic pair potentials similar to those of Fig. 1. (b) The A particle incoherent intermediate scattering function for the same family of potentials as a function of time at the wavevector defined from the maximum of $g(r)$. For comparison the dotted line shows the WCA prediction [12]. (c) The function $\chi_4(t)$ for the A particles for the same pair potentials, including the WCA prediction (dotted line).

The single-component LJ system does not have a broad

dynamic range because it cannot be deeply supercooled. To test the robustness of the predicted invariance of the physics for families of isomorphic pair potentials, we simulated also the Kob-Andersen binary LJ (KABLJ) mixture [13] that is easily supercooled into the highly viscous state. For this system the constant $\alpha = 1.29$ was identified from simulations of 1,000 particles at the reference state point $(\rho, T) = (1.60, 2.00)$, using again Eq. (3). From the function $h(\rho)$ a family of isomorphic equivalent pair potentials was generated much like those of Fig. 1; in particular some of them have a vanishingly small attraction.

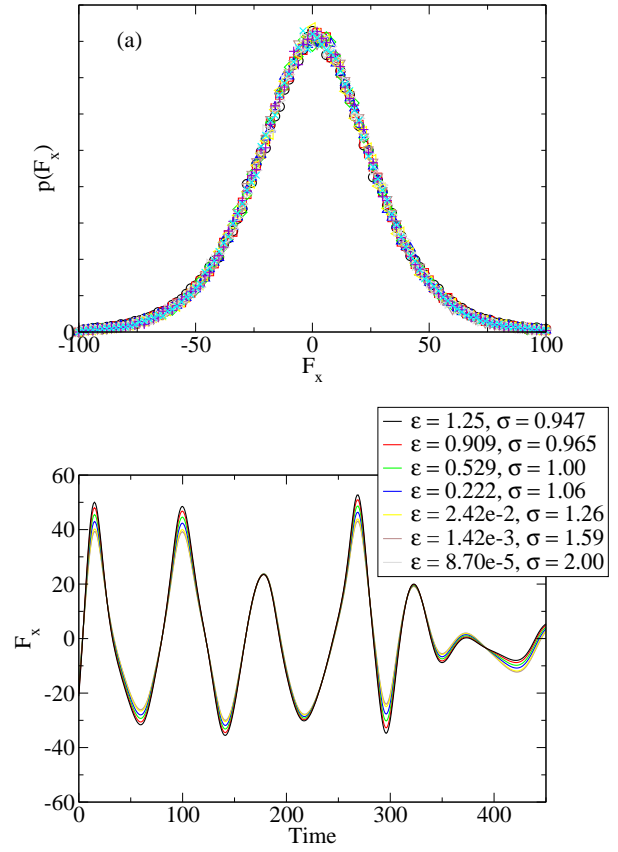


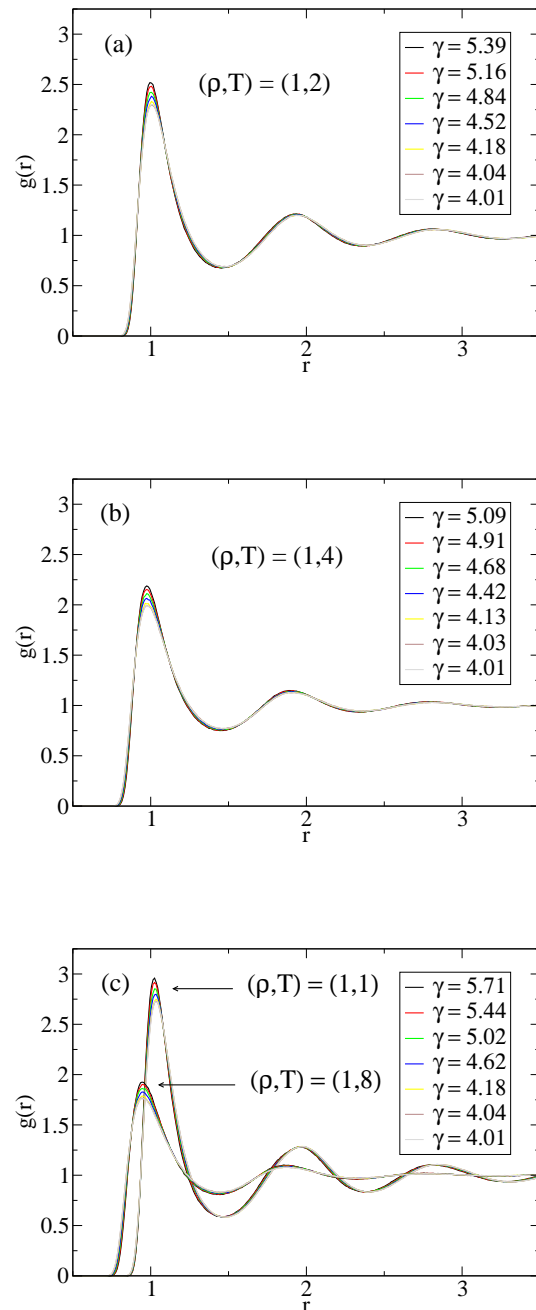
FIG. 4: (a) Distribution of forces for the different single-component LJ potentials of Fig. 1 at the state point $(\rho, T) = (1, 1)$, based on seven independent simulations of the seven potentials. (b) Snapshot of the x -component of the force F_x on one particle as a function of time. The system simulated is defined by $\epsilon = 1.25$ and $\sigma = 0.947$; F_x was subsequently evaluated for the same series of configurations for the six other potentials. These figures show that, even though the pair potentials are quite different, the forces are virtually identical (except at the extrema).

Figure 3(a) shows the AA particle radial distribution functions for these different pair potentials. Figure 3(b) shows the A particle incoherent intermediate scattering function; we here included simulations of the Weeks-Chandler-Andersen (WCA) system for $\epsilon = 1.25$ and $\sigma = 0.947$ (dotted line). Even though the WCA approximation has the correct repulsive forces, its physics differs considerably from the isomorphic pair potentials [12], some of which have also (virtually) no attractions. We also calculated $\chi_4(t)$, a measure of dynamic heterogeneities. The results shown in Fig. 3(c) are more noisy, but confirm the predicted invariance of the dynamics for the different pair potentials.

It would require extraordinary abilities to know from inspection of Fig. 1 that these pair potentials have virtually the same structure and dynamics. The potentials have neither the repulsive nor the attractive terms in common, so why is it that they have such similar behavior? The simple answer is that they result in virtually the same *forces* (Fig. 4). The point is that the force on a given particle is a sum of contributions from (primarily) its nearest neighbors, so plotting merely the pair potential can be misleading. Thus, by reference to the pair potential alone, one cannot identify separate roles for the repulsive and the attractive forces in a many-particle system; there simply are no “repulsive” and “attractive” forces as such.

Separate from illuminating in which sense specific roles

are played by the repulsive and attractive parts of the pair potential [14], the data presented in this paper support an interesting approximate scaling principle proposed in 2003 by Young and Andersen [15]. According to this, two liquids at the same temperature and density with the same particle mass have the same dynamic correlation functions if the static pair correlation functions are the same. Another way of saying it this that for fixed density, particle mass, and temperature, the dynamic correlation functions are functionals of the radial distribution functions.



The above reported simulations focussed for each system on one particular state point. If the potentials in Fig. 1 are really to be regarded as equivalent with respect to structure and dynamics, however, one should test also other state points. We have done this briefly for the single-component LJ liquid of Fig. 1. The results are shown in Fig. 5, where temperature was increased significantly. Clearly, the degree of similarity observed at the state point $(\rho, T) = (1, 1)$ is maintained also for the other state points (for comparison Fig. 5(c) reproduces the $(\rho, T) = (1, 1)$ results from the left panel of Fig. 2(a)).

FIG. 5: Radial distribution functions for the potentials of Fig. 1 at other state points than the state point $(\rho, T) = (1, 1)$ studied above. For reference we give in each subfigure the value of γ defined in Eq. (3). (a) $(\rho, T) = (1, 2)$; (b) $(\rho, T) = (1, 4)$; (c) $(\rho, T) = (1, 8)$ – the γ 's reported here are those of the state point $(\rho, T) = (1, 1)$.

The centre for viscous liquid dynamics “Glass and Time” is sponsored by the Danish National Research Foundation (DNRF).

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